compostible. The casing must be sufficiently permeable and usable for virtually all types of sausage, inter alia, therefore, for the production of cooked-meat sausages and scalded-emulsion sausages, and also of raw sausages.

The object is achieved by a blend of thermoplastic starch or a thermoplastic starch derivative and one or more synthetic polymers. The present application thus relates to a seamless tubular food casing which is blown in an area ratio of from 1:2 to 1:10, is produced from a thermoplastic mixture which comprises a) thermoplastic starch and/or a thermoplastic starch derivative and b) at least one other polymer obtainable by polycondensation or polyaddition, the weight ratio a):b) being in the range from 90:10 to 10:90.

The thermoplastic starch derivative is preferably a starch ester as described extensively in DE-A 195 15 477. The acid component in the ester is generally a (C_2-C_{10}) alkanoic acid which is preferably unbranched or branched only to a small extent. A particularly preferable and inexpensive starch alkanoate is starch acetate, in particular that having a degree of substitution less than 3, specifically from 1.5 to 2.4. Starch esters, such as starch acetate, which are different from starch itself, are already thermoplastic as such and do not need to be plasticized first. Starch esters having a relatively long alkyl chain, for example starch hexanoates, starch octanoates or starch decanoates, cause a change in the suppleness and toughness and also the permeation of the food casings. By combining different starch esters, casings having quite specific properties may be produced. Thermoplastic starch derivatives which have cationic quaternary side groups containing hydrophobic (C_2-C_{18}) alkyl groups, preferably (C_2-C_{12}) alkyl groups, are also suitable.

It has been found that food casings which consist only of thermoplastic starch and/or thermoplastic starch derivatives still do not have the desired level of extensibility,

strength, toughness, suppleness, but also primarily stability to hot or boiling water. The properties of the casing were not improved significantly even when other low-molecular-weight substances, such as lubricants, plasticizers and fillers, were added to the thermoplastic starch or the thermoplastic starch derivative. Surprisingly, it has been found that significant improvement does not occur until the thermoplastic starch or the starch derivative is blended with other polymers which are obtainable by polycondensation or polyaddition and are safe for food packaging.

The polymer obtainable by polycondensation is preferably a homopolymer or copolymer containing hydroxycarboxylic acid units. Particularly preferably it is a polylactide, poly(3-hydroxypropionic acid), poly(3-hydroxybutyric acid), poly(4-hydroxybutyric acid), polycaprolactone, polyesterurethanes, polyetherurethanes and polyesteretherurethanes. Polyalkylene carbonates of the formula $-[CHR^1-CHR^2-O-CO-O-]_n$, where R^1 and R^2 independently of one another are a hydrogen atom or a (C_1-C_4) alkyl radical and n is an integer from 10 to 5000. Particularly suitable polyalkylene carbonates are polyethylene carbonate ($R^1=R^2=H$) and polypropylene carbonate and mixtures thereof. The polyalkylene carbonates are described, for example, in WO 96/35746. A preferred polymer which is obtainable by polyaddition is polyvinyl acetate. The polycondensation or polyaddition products may be prepared synthetically by known processes. They are usually not crosslinked or crosslinked only to a small extent. Their mean molecular weight M_w is generally from 20,000 to 2,000,000, preferably from 100,000 to 1,000,000. It is assumed that the polycondensates form a type of matrix in which the thermoplastic and thus non-structured starch or the starch derivative is uniformly distributed.

The weight ratio of the components a):b) is preferably from 20:80 to 80:20, particularly preferably from 40:60 to 60:40.

In addition to the components a) and b), the thermoplastic mixture can further comprise other low-molecular-weight or high-molecular-weight constituents which act in particular as plasticizers or lubricants or improve the compatibility of the components with one another. As a result of the further constituents the homogeneity or flowability of the extrudable thermoplastic mixture can if appropriate be further improved. Suitable plasticizers are particularly glycerol, diglycerol, sorbitol, polyethylene glycol (PEG), citric acid triethyl ester, acetylcitric acid triethyl ester, glycerol triacetate, phthalic esters (especially dimethyl phthalate, diethyl phthalate and dibutyl phthalate) and sorbitol monoesters and diesters. The proportion of plasticizer(s) is up to 30% by weight, preferably up to 15% by weight, in each case based on the total weight of the thermoplastic mixture. Lubricants which improve the homogeneity of the thermoplastic mixture are, in particular, vegetable fats or oils, synthetic triglycerides, lecithins, ethoxylated fatty alcohols or waxes. The proportion of lubricants is up to 12% by weight, preferably from 2 to 6% by weight, particularly preferably from 3 to 6% by weight, in each case based on the total weight of the mixture.

The casing of the invention can finally further be reinforced with fibers. Generally, the fibers are relatively short (on average about 0.1 to 3 mm, preferably from 0.2 to 1.5 mm). In order that the casing remains biodegradable and thus compostible, fibers of cotton linters, wood pulp, regenerated cellulose ("regenerated fibers"), of hemp, flax, sisal or jute are particularly suitable. The proportion of fibers can be up to 25% by weight.

Preferably, the fiber content is from 2 to 15, in particular from 5 to 15, % by weight, in each case based on the total weight of the mixture. The fibers are uniformly distributed in the thermoplastic mixture or the extrudable melt produced therefrom.

The casing can further contain fillers, either instead of the fibers or additionally. Suitable fillers are, for example, calcium carbonate, talc, kaolin or anhydride (= calcium sulfate). The proportion of fillers can be up to 12% by weight, but preferably it is from 2 to 8% by weight, particularly preferably from 4 to 8% by weight, in each case based on the total weight of the thermoplastic mixture.

For casings having a particularly high stability to hot or boiling water it has proved to be expedient also to add crosslinkers to the thermoplastic mixture. Suitable crosslinkers are, for example, dicarboxylic acids, diisocyanates or triisocyanates (particularly hexamethylene diisocyanate), dialdehydes (particularly glyoxal), diepoxides, diimines or silanes or siloxanes containing vinyl group(s), for example vinyltrimethylsilane. The crosslinker is preferably not added until the remaining components of the mixture are already molten. The proportion of crosslinker(s) is up to 20% by weight, preferably from 0.5 to 10% by weight, particularly preferably from 1 to 5% by weight, in each case based on the total weight of thermoplastic mixture.

The production of thermoplastic starch is known and described in WO 90/05161 and 90/10019. During the plasticization, the helix structure of the native starch is destroyed. The starch is thereafter in an amorphous state. The plasticization is generally performed by heating and supplying mechanical energy, for example by relatively long thermal treatment in a kneader or in a single- or double-screw extruder. In order that the starch melts below its decomposition temperature, additives are necessary, such as water, 1,3-butanediol, glycerol, diglycerol, N,N-dimethylurea, sorbitol or citrate. In the case of plasticization using water, from about 20 to 25% by weight of water, preferably about 17% by weight of water, are added, in each case based on the weight of the native starch. A temperature of from about 100 to 130°C is maintained in the course of this. In the case of plasticiz-

ation using glycerol, a proportion of from 0.5 to 20% by weight, preferably from 8 to 16% by weight, again in each case based on the weight of the native starch, and a temperature of from 150 to 170°C have proved expedient. Owing to this treatment, the proportion of crystalline starch is decreased to 5% by weight or even less.

The thermoplastic mixture may be prepared from said components in conventional apparatuses, for example in a double-screw kneader. To form a homogeneous, thermoplastic melt from the mixture, a temperature of from 90 to 200°C, preferably from 120 to 180°C, has proved to be expedient. The melt can be extruded, comminuted after cooling and stored temporarily as granules or in similar form or equally well be processed directly to a food casing. The tube produced from the described melt is then expanded with air in the blown film extrusion process and stretched longitudinally and transversely in an area ratio of from 1:2 to 1:10, preferably from 1:3 to 1:5. Not until the stretching do the tubes achieve the optimum strength, elongation, caliber constancy and shrinkage. The extent to which each of these properties is expressed primarily depends on the composition of the thermoplastic mixture. Thus the food casings, by a targeted selection of the components of the thermoplastic mixture, the stretching conditions and the type of post-treatment, can be adapted to the most varied requirements. If appropriate, the blown casings can also in some cases be thermoset.

In a further process step, preparations can be applied to the tubular casings internally and/or externally in order to make them still more suitable for the various applications as sausage casing. For this there may be used most liquid preparations which are also customary for the surface finishing of cellulose hydrate casings, in a concentration adapted accordingly. Thus, it is particularly expedient to coat with protein (preferably casein, gelatin, soy protein or wheat protein) the inner surface of a casing intended for

long-keeping sausage. The protein is customarily in this case bound to the casing surface using an aldehyde. By using resins or by adding release agents to the protein/aldehyde, the peelability of the sausage casing can be set. The adhesion of the casing to the sausagemeat emulsion may be reduced to a strong release action using known formulations (this is required, for example, in the case of Thüringer Blutwurst).

Suitable external preparations are also already known from cellulose casings. By treating the outer surface of the casing with such a preparation, in particular, mold resistance, surface roughness and printability may be set.

The food casing of the invention can have its properties varied to the extent that it corresponds to a cellulose casing or a plastic casing. It may be produced by simple and environmentally compatible processes. Its good swelling and shrinkage properties means that it always lies tightly against the sausagemeat emulsion and that no creases form even during slow drying. By a selection of the components, the permeability of the casing for water, water vapor and oxygen can be set exactly. Surprisingly, the casing is even permeable for smoke, so that it is also readily suitable for smoked sausage types (for example salami). The starch used for producing the casing furthermore is a particularly expedient renewable raw material.

The casing of the invention can finally also be enclosed by a, preferably broad-mesh net, which imparts a particularly attractive appearance to the finished product. It consists of a tubular net which is known for wrapping sausages and is adapted to the periphery of the carrier tube. The thickness shall be at least ... mm, so that the net stands out clearly. Very different mesh shapes are used: triangular, hexagonal, square, diamond-shaped, round or oval. The meshes themselves are formed from individual filaments or filaments entwined together and usually consist of textile filaments, preferably

of a material which resembles the carrier tube. In contrast to the net disclosed by DE-A 39 07 951, adhesive is no longer required, since the casing of the invention adapts to the net structure and thus ensures the desired adhesion.

In the examples hereinafter, percentages are percentages by weight, unless stated otherwise.

<u>Example 1:</u>

a) Production of thermoplastic starch
100 kg of potato starch were dried under reduced pressure to a water content less than 0.3% and melted together with 50 kg of glycerol (99% pure) in a kneader at from 160 to 190°C and mixed well. To destroy the helix structure of the starch, the melt was kept at 170°C for about 2 h. It was then extruded and granulated. During subsequent storage of the granules, the starch remained in the amorphous and thus thermoplastic stage.

b) Production of an unreinforced seamless food casing:
75 kg of the granules described under a) (50 kg of starch + 25 kg of glycerol) were mixed with 50 kg of polycaprolactone, 3 kg of sunflower seed oil and 3 kg of hexamethylene diisocyanate. The components which were evenly mixed with one another were melted in an extruder at 150°C. The melt was then extruded through an annular die. The diameter of the annular die was chosen so that after the film blowing in an area ratio 1:10 a tube having a diameter of 60 mm (= caliber 60) and a wall thickness of 80 ìm was obtained.

The tubes are stable in water, but swell therein and shrink again on drying. They can be placed on the stuffing apparatus in the form of sections tied-off at one end or in a consolidated form as what are termed "shirred sticks". They are suitable in particular as casings for long-keeping sausage (that is for a raw sausage having a particularly high degree of maturation).

In the water-impregnated state, a bursting pressure of from 25 to 35 kilopascals (kPa) was achieved. The static elongation at 15 kPa internal pressure was from 68 to 76 mm. The casings were stuffed with salami emulsion. The adhesion to the emulsion was low (peelability after 2 weeks: "1" on a scoring scale from 1 to 6, where "1" is very easily peelable" and "6" is "excessively strong adhesion, casing cannot be removed without damage").

To increase the emulsion adhesion, therefore, a protein (casein)/glyoxal internal preparation was applied, as is customary with cellulose hydrate tubes.

Example 2:

A blend was produced from 50 kg of starch acetate having a degree of substitution of 2.2 and a molar mass of 580 g/mol which was mixed with 50 kg of polyethylene carbonate having a molecular weight M_w of 500,000 and 15 kg of citric acid triethyl ester were added. To this mixture was added 8 kg of thermoplastic starch, 5 kg of 1,2:5,6-diepoxyhexane (hexamethylene diepoxide) and 5 kg of ethoxylated octadecanol (stearyl alcohol), on average 12 ethylene oxide units.

This mixture was melted at from 150 to 170°C in a double-screw extruder, mixed well and then extruded through an annular die whose dimensions were selected such that after blown film extrusion in an area ratio of 1:8 a tube of caliber 70 having a wall thickness of 90 ìm was obtained.

The tube thus produced was resistant to simmering; it swelled in water and shrank again on drying.

In the water-impregnated state, a bursting pressure of from 38 to 42 kPa was achieved. The static elongation at 15 kPa internal pressure was from 76 to 80 mm.

Sections tied off at one end or shirred were suitable for producing long-keeping sausage and scalded-emulsion sausage. The peelability was good with both types of sausage (score: 2).

Example 3 (Production of a fiber-reinforced casing):

A blend of 50 kg of starch acetate, 15 kg of citric acid triethyl ester and 50 kg of polyethylene carbonate was mixed uniformly in the melt with 10 kg of flax fibers of length from 0.2 to 1.5 mm. The melt was extruded through an annular die at from 160 to 180°C and blown (area stretching ratio 1:6), so that a tube of caliber 60 was obtained. The water-impregnated tubes achieved a bursting pressure of from 60 to 65 kPa and a static elongation of from 65 to 70 mm at 21 kPa internal pressure.

The casings could be used for scalded-emulsion sausage and long-keeping sausage. They achieved a stuffing caliber of from 66 to 68 mm and could be peeled easily.

Example 4:

A polymer blend as described in Example 1 was evenly mixed in the melt with 12% cotton linters, extruded and blown via an annular die, so that at a longitudinal and transverse stretching in an area ratio of 1:10 a tube of caliber 50 was obtained.

In the water-impregnated state, a bursting pressure of from 60 to 68 kPa was measured and a static elongation of from 56 to 62 mm at 21 kPa internal pressure was measured.

The stuffing caliber for scalded-emulsion sausage and long-keeping sausage was from 57 to 62 mm. The peelability was good.